# Investigation of GaAs nanowires grown via MOVPE using the Vapour−Liquid−Solid technique

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One−dimensional semiconductor nanowires are a subject of intensive research primarily due to their novel optical and opto−electronic properties [1−5]. Typically these nanowires have diameters in the range of tens of nanometers with lengths of a few to tens of micrometers. Over the past few years there has been considerable effort directed towards the synthesis of nanowires in a variety of semiconductors using techniques such as laser ablation, processes based on the vapour−liquid−solid (VLS) mechanism [4,5] and other methods. Recently nanowire devices such as resonant tunneling diodes [6] and electrically−driven single−wire lasers [7] have been reported. The electronic and optical properties of the nanowires are critically dependent on their dimensions and crystal structure. As even small changes in the size and crystalline perfection of a nanowire can significantly influence device performance, the growth of defect−free nanowires is key to improved nanoscale devices. In this work we report on GaAs nanowires grown on Si and GaAs substrates via metal−organic vapour phase epitaxy (MOVPE) using the vapour−liquid−solid (VLS) mechanism. These nanowires typically exhibit a circular cross−section with diameters ranging from 10 nm − 40 nm. We also present a study of the defect structure of GaAs nanowires using transmission electron microscopy which suggests a critical diameter for the formation of twinning defects in VLS−grown GaAs nanowires.

The VLS mechanism, developed in the early 1960s [8], is an anisotropic growth process promoted by the presence of a liquid alloy which acts as a catalyst for the growth of nanowires. Gold is commonly used since it forms eutectic alloys with Si, Ga, at temperatures of ~350°C [4]. In this work a thin film of gold (0.5−2nm) was deposited on nominally (100) oriented Si/GaAs substrates by vacuum evaporation. After deposition, the substrate was transferred to the MOVPE reactor and annealed at 500°C for 5 minutes in an $H_2$ /$AsH_3$ atmosphere. This results in self−aggregation of the gold film into a dense collection of small islands distributed on the substrate surface. For ~1.5nm thick layers, atomic force microscopy measurements show islands of height ~5nm and density ~ 400 /$\mu m^2$ , with a spread in diameter between 15 and 40 nm after annealing. The nanowires are grown in a low−pressure (76 torr) horizontal MOVPE reactor (CVD Inc.) using trimethylgallium, TMGa, (flow rate 100 torr−cc/min) and AsH3 (10 sccm) precursors. The V/III ratio is ~76 and the growth temperature has been varied from 450°C−550°C. The surface of each liquid droplet of the Au/Si eutectic act as a preferred site for the absorption of Ga and As atoms from the vapour phase. With increasing concentration of the precursors, the liquid droplets, eventually become supersaturated and start precipitating the GaAs compound at the liquid/substrate interface leading to the growth of the GaAs nanowires.

Subsequent to growth, the GaAs nanowires have been characterized by high resolution scanning electron microscopy (SEM) in a FEI/Philips Sirion SEM equipped with a FEG source and by transmission electron microscopy (TEM) in a FEI/Philips CM200 TEM operating at 200kV. While the SEM studies have been carried out on as−grown nanowires attached to the Si substrate, the TEM studies have been carried out on nanowires detached from the Si substrate and placed on a carbon−coated 3 mm copper grid. Since the diameter of these nanowires ranged from 10 nm − 40 nm, no further sample preparation was required for the TEM studies.

Fig. 1 shows the SEM top−view of the as−grown GaAs nanowires on Si. A high density of intertwined nanowires is visible in this micrograph. In addition, the inset shows the gold island at the tip of a nanowire as seen in a bright field TEM micrograph. Figs. 2(a) and (b) show two SEM micrographs recorded at identical magnifications looking

near−parallel to the substrate. Fig. 2(a) shows a region nearer to the substrate, which shows short, fractured nanowires while Fig. 2(b) shows a region further away from the substrate where the wires are longer and exhibit large plastic deformations. It should be noted that most of the GaAs nanowires visible in Fig. 2(a) are thicker than those shown in Fig. 2(b). This indicates a possible relationship between the diameter of the GaAs nanowires and their mechanical properties.

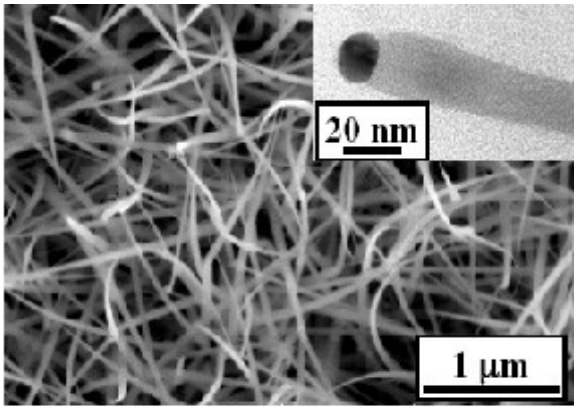


Fig. 1: SEM image of GaAs nanowires. Inset: TEM image showing the gold island at the tip of the nanowire

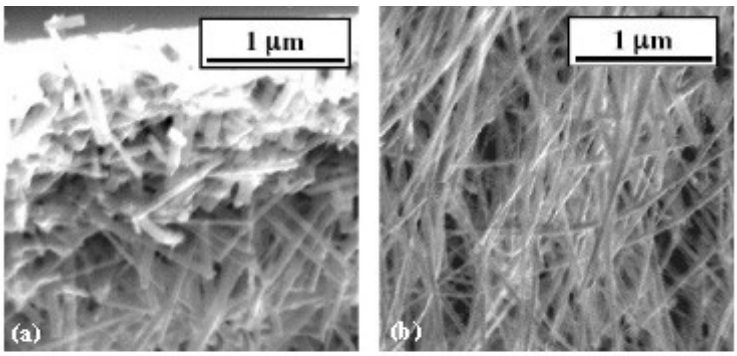


Fig. 2: SEM images of two different regions showing- (a) thicker and shorter wires near substrate and (b) thinner and longer wires further away from substrate

TEM studies on the nanowires indicate that the wires predominantly exhibit the diamond cubic structure with the growth axis parallel to <111>. Further, a high density of twin defects aligned perpendicular to the growth axis is visible. Electron diffraction patterns from the nanowires clearly show additional reflections arising from a twinned orientation in addition to the fundamental matrix reflection. The diffraction patterns from all the nanowires sampled on the TEM grid could be indexed based on the diamond cubic structure of GaAs, and they were aligned with their growth directions parallel to <111>. While the relatively thicker GaAs nanowires exhibited a high density of twins, the thinner ones however did not show twin formation. This is demonstrated using a selected set of bright−field TEM images shown in Fig. 3. Each of these images is from a different nanowire and the average diameter of the nanowires gradually decreases from (a) to (f). While twins are clearly visible in Figs. 3 (a)−(d), no such defects are seen in the thinner wires in Figs. 3(e) and (f). Therefore, it appears that there is a critical diameter for twin formation in these GaAs nanowires. Based on these TEM observations, the critical diameter appears to be ~ 20 nm. (As the wires taper slightly towards the tip, the diameter of the nanowires varies along their length and it is however rather difficult to exactly specify a value for the critical diameter). Nanowires with diameters less than ~20 nm did not exhibit twin formation which also suggests an explanation for why only the thinner nanowires are long and ductile. The observation of a critical diameter for twin formation in GaAs nanowires is likely to be technologically quite important as the optoelectronic properties of the nanowires would be enhanced in the absence of defects.

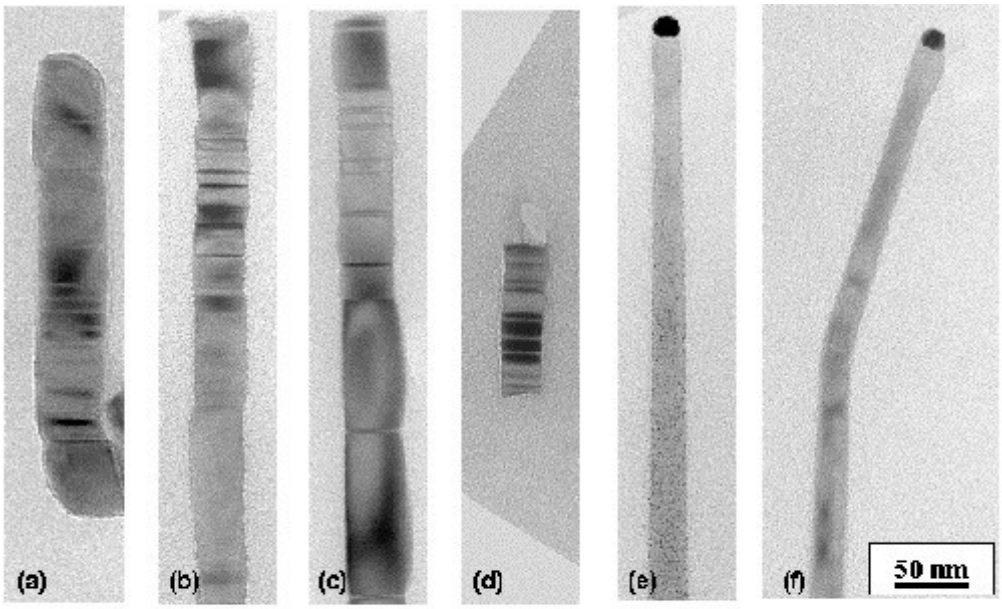


Fig. 3: Series of TEM images showing GaAs nanowires of progressively reducing average diameters. Nanowires in (e) and (f) do not show twins.

In summary, GaAs nanowires have been grown on GaAs and Si substrates via the VLS mechanism, and their structure investigated in detail using SEM and TEM. These nanowires exhibit the diamond cubic crystal structure and a <111> growth direction. Extensive twinning is observed in relatively thicker nanowires and there appears to be a critical diameter of ~ 20 nm below which the GaAs nanowires do not exhibit twin formation. We believe these observations may have important implications for the development of nanowire devices.

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